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Japanese Laid-Open Patent

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Applicant: Shunnpei Yamazaki

1. Title of the Invention

Semiconductor Device

2. Scope of the Claim

1. A semiconductor device, characterized by the provision of at least two non-single-crystalline semiconductors o a substrate, having different energy bands that are continued or substantially continued in a boundary or a boundary region by changing the stoichiometric ratio of said semiconductor layers.

2. The semiconductor device according to claim 1, characterized in that the semiconductors have at least one of PN junction, PI junction, NI junction, PP junction, NN junction, II junction, and Schottky junction therein.

3. The semiconductor device according to claim 1, wherein the energy band of the semiconductor layers which develops photoelectromotive force is gradually reduced or substantially gradually reduced from a surface of the semiconductor layers onto which a light is irradiated toward a depthwise direction

thereof.

3. Detailed Description of the Invention

The present invention relates to a semiconductor device, characterized by the provision of two non-single-crystalline semiconductors having different energy bands (for simplicity, energy band is hereinafter referred to as Eg, which is also used hereinafter to mean energy band width or energy gap), the conductive band (hereinafter referred to as CB) or valence band (hereinafter referred to as VB) of which being continuous or substantially continuous in a boundary or boundary region of the semiconductors by changing the stoichiometric ratio of two semiconductors.

The present invention relates to a semiconductor device in which non-single-crystalline semiconductors of the same conductivity type or of different conductivity types are junctioned so as to emit a light or, to the contrary, so as to develop a photoelectromotive force when the light is irradiated onto the junction.

The present invention relates to a semiconductor device which is produced by providing the non-single-crystalline semiconductors on a flexible film-type substrate and which, thus, can be continuously mass-produced at a low cost.

The present invention relates to a semiconductor device, in a boundary or boundary region of which two semiconductors having different energy bands have a junction of different

conductivity type such as PN junction, PI junction, NI junction, and Schottky junction, and a junction of the same conductivity type such as NN junction, PP junction, and II junction, or multiple junction thereof.

Further, the present invention relates to a semiconductor device with photoelectric effect which develops photoelectromotive force when light is irradiated onto the junction portion and which forms a photo cell, in particular, a solar cell, or, which emits visible light of a specific wavelength or white light when electric current flows in the junction portion.

The present invention relates to a semiconductor device comprising two semiconductors which device does not have specific interface states caused by boundary or junction therein or in which the interface states are practically electrically negligible and substantially does not exist at or near the boundary of the two semiconductors, or at or near PN junction, PI junction NI junction, Schottky junction, or multiple junction thereof. Still further, the present invention relates to a semiconductor device to which, in order to attain the above, hydrogen such as hydrogen and deuterium or halogenide such as chlorine and bromine is added at the concentration of 0.1 to 200% so as to neutralize or balance the interface states or the recombination center of charge.

According to the present invention, the two non-single-

crystalline semiconductors are a semiconductor such as silicon and germanium, a group IV-IV compound semiconductor such as silicon carbide, germanium carbide, and germanium silicide, or a group III-V compound semiconductor such as GaAs, GaAlAs, GaP, and BP.

Further, according to the present invention, at least two of the above semiconductors having different Eg are stoichiometrically mixed to make CB or VB be continuous in view of energy. In addition, the present invention relates to a semiconductor device in which carbon, hydrogen, or nitrogen of an amount stoichiometrically determined to some extent as a dopant is added at the boundary or boundary region.

Conventionally, when single-crystalline semiconductors having different energy band are junctioned, what is called hetero-junction is formed at the boundary. For example, when GaP and GaAs are junctioned, since both of them are single-crystalline, unconformable stepwise hetero-junction shown in Fig. 1 is formed on the surface of the two energy gaps (hereinafter referred to as Egs). Due to the unconformity, when, for example, $Ga_{0.3}Al_{0.7}As$ (1) and GaAs (2) are junctioned, not only a notch (3) and a jump (4) but also interface states (5) are generated. Due to the interface states (hereinafter referred to as Ns), at the junction portion, carrier as an electron or a hole is recombined through Ns and is lost.

As a result, a conventional semiconductor device has

serious problems that the lifetime of carriers is shortened and that, when a semiconductor device employing the junction is used to attain a specific action such as development of photoelectromotive force, charge excited by light is lost before it develops photoelectromotive force. In addition, when the semiconductor device is used to emit light making use of electric current flow, since an electron and a hole recombine via the interface states, which is referred to as indirect transition, there is a serious problem that visible light is not emitted and only heat is generated. Further, when characteristics of PN junction diode are required, since the withstand pressure of reverse direction characteristics is small, the semiconductor device is merely a soft-break-down-type diode. Fig. 1(A) shows a case of NP junction. Fig. 1(B) shows a case of NN junction. In the case of Fig. 1(B), there is a serious problem that, in addition to Ns (7), a spike (6) is generated which is a barrier to movement of electrons. According to the present invention, such a notch, a jump, and a spike are prevented. The object of the present invention is to vary, in view of energy, continuously one or both of CB and VB of the energy band at this junction portion. Further, the present invention is characterized in that Ns caused by dangling bonds and crystal defects which inevitably exist due to lattice defects on the surface of conventional hetero-junction is removed or extremely reduced.

Since a semiconductor device according to the present invention is structured to have continuous junction in view of energy band, such a semiconductor device can extremely rapidly develop into a new semiconductor device utilizing the difference of the energy bands.

The present invention is now described in the following with reference to embodiments.

The base of the present invention is to disperse stoichiometrically evenly each component of an amorphous (genuine amorphous or polycrystalline in the short range order of 5 to 100 Å) semiconductor having one conductivity type and a polycrystalline semiconductor in which crystals are above 100 Å having one conductivity type (these two kinds of semiconductors are hereinafter generically referred to as non-single-crystalline semiconductors) made of, for example, silicon, germanium, or silicon carbide, or each component of one of the above semiconductors and a compound semiconductor such as GaAlAs. Here, even dispersion means that stoichiometric waves of the components are in the direction of locally interacting with each other. It is necessary for the non-single-crystalline semiconductors to have two waves that are even, and have the enough regularity or the characteristics of a crystal to determine Eg. An embodiment of the present invention is now described in the following.

In the present embodiment, the used substrate is either

what is called a hard substrate made of, for example, metal, semiconductor, insulator, or a composite of insulator such as glass and ceramic and, for example, a metal film with which the insulator is partially or totally coated, or, a flexible film-type substrate the thickness of which is 0.2 to 200 μ, in particular 1 to 10 μ made of, for example, FEP plastics, Kapton, Mylar, polyimide, celluloid, vinyl chloride, or polyurethane or composite substrate of the above flexible film-type substrate and a metal film with which the substrate is coated (what is called a soft substrate). (In the present embodiment, the above substrates are generically referred to as a substrate.) The flexible film-type substrate (soft substrate) has characteristics that it can be in the shape of a roll in mass-production and the cost of the material of the substrate is very low. In addition, in case of a single-crystalline semiconductor layer, when it is made in the shape of a roll or when they are conveyed, its reliability may be spoiled by, for example, cracking, while in case of a semiconductor layer according to the present invention, since it is non-single-crystalline such as amorphous, they are flexible and thus ideal. In the embodiment of the present invention, for example, silicon is formed on the substrate in a layer structure, that is, as a coat, using silicide gas such as silane and dichlorosilane. In order to attain this, on the inlet side of a reactor made of heat-resisting glass such as

quartz or stainless steel, silicide gas such as silane and dichlorosilane, carrier gas such as hydrogen and hydrogen chloride, and a dopant which determines the conductivity of N type semiconductor such as phosphorus and arsenic using phosphine or arsine or a dopant which determines the conductivity of P type semiconductor such as aluminum, gallium, and boron using aluminum chloride, gallium chloride, or diborane are introduced. In addition, carbide, nitride, and oxide gases such as methane, ammonia, and oxygen can be fed. The gases in the reactor are exhausted by a vacuum pump, which can evacuate the reactor up to 0.001 torr. A substrate supported by a susceptor was inserted into the reactor. Next, the reactor was evacuated to 0.1 to 10 torr. Then, the substrate was heated by high-frequency heating of 1 to 50 MHz or by such high-frequency heating in conjunction with radiation heating to excite or decompose the reactive gases. The high-frequency energy was given so as to promote voltage excitation to chemically sufficiently excite bonds of the dopants or of the semiconductor material. The reactive gases formed a coat on the substrate. Here, depending on the temperature of the substrate, the coat was amorphous when the temperature was the room temperature to 500°C and was polycrystalline when the temperature was 350°C to 900°C. When the substrate is monocrystalline and the coat on the substrate grows as an epitaxial layer with the temperature being above 900°C, the

coat is single-crystalline. Experiments proved that it was impossible to make such a single-crystalline semiconductor to have the structure of the present invention. The primary feature of the present invention is to use a non-single-crystalline coat. If a dopant such as phosphorus and arsenic which shows N type conductivity in a semiconductor is doped in the non-single-crystalline coat using phosphine (PH_3) or arsine (AsH_3) at the concentration of 10^{14} to $5 \times 10^{22} cm^{-3}$, an N type semiconductor is obtained.

On the other hand, if aluminum chloride ($AlCl_3$), gallium chloride ($GaCl_3$), or diborane (B_2H_6) at the above concentration is doped, a P type semiconductor is obtained. The dopants of the above two conductivity types were doped at the same time and introduction of the silicide gas was decreased or stopped as necessity requires to form a compound semiconductor, and a boundary region of the present invention where Eg was continuous was provided between the two semiconductors. Further, in case these dopants were not at all doped, the semiconductors became intrinsic or substantially intrinsic by being contaminated with impurity at the background level of the device. Hydrogen, deuterium or halogenide such as chlorine is added to the non-single-crystalline coat at the concentration of 0.2 to 200% in addition to the material forming the semiconductors, i. e., silicon.

They bond to dangling bonds which tend to remain after the

semiconductor layer is formed to suppress the generation of recombination center and have an action of electrical neutralization (inactivation). This addition of hydrogen or halogenide at the same time when the semiconductor layer was formed or after the coat was formed was a quite important element to put the present invention to industrially practical use.

With respect to the latter, dangling bonds were excited by high-frequency energy or microwave energy after the coat was formed, and then, hydrogen and so on which was made chemically active was added in the coat. Practically, the device of the present invention including a substrate and a semiconductor layer provided thereon was inserted to atmosphere such as hydrogen, the above-mentioned electrical energy was given to activate (excite) the atmosphere such as hydrogen, and the temperature was raised up to 500°C.

According to the present embodiment, the dopants which determine the conductivity type of either P type or N type and impurity such as hydrogen and halogenide were added by activating the hydrogen or halogenide at the same time as the reactive gas was electrically activated.

Of course, it is needless to say that, as disclosed in Japanese Patent Application No. SHO 53-86867 and 53-86868 (both invented by the inventor of the present invention), the semiconductor layer may be annealed with active hydrogen after

the semiconductor layer is formed. Further, in the present embodiment of the invention, carbon, nitrogen, and oxygen were evenly dispersed and added to the semiconductor. CH_4 and C_2H_6 were used to add carbon. Ammonia (NH_3) and hydrazine (N_2H_4) were used to add nitrogen. H_2O or O_2 were used to add oxygen. With regard to addition of mixture of the above, N_2O, NO_2, alcohols such as CH_3OH, CO_2, and CO may be inserted into the reactor using a carrier gas of oxygen or chlorine to add two or more of the above, for example, nitrogen and oxygen, or carbon and oxygen. Conventionally, when oxygen, nitrogen, and so on was added after a single-crystalline semiconductor coat was formed, the results were that silicon oxide (Eg=8eV) or silicon nitride (Eg=5.5eV) were obtained, which were merely insulators. However, when these were added either electrically or, using electrical energy of high-frequency or microwave in conjunction with heat, at the same time when the silicon coat was formed, the energy band of the semiconductor could be of an intermediate value between 1.1 eV and 3 eV (in case of SiC), 5.5 eV (Si_2N_4), or 8 eV (SiO_2) according to the stoichiometric ratio of those which were added. The value of Eg of the coat was measured by photoluminescence or light excitation.

With the compound semiconductor, by varying the stoichiometric mixture ratio of Ga, Al, P, and As, the value of Eg

could be arbitrarily decided between 1.3 eV and 3.5 eV (for example, GaAs 1.4 eV, GaAsP 1.9 eV, $GaPI_n$ 2.3 eV, and $AlPI_n$ 2.3 eV). Since both of such a compound semiconductor and another such compound semiconductor or both of such compound semiconductor and a semiconductor made of a single element such as silicon were non-single-crystalline semiconductors, there was no specific Ns existing only on the interface which was in, for example, hetero-junction. Further, the conductive band (CB) and valence band (VB) of the energy band of the semiconductor device using the semiconductors could be formed continuously stepwise (substantially continuously) or smoothly continuously (continuously).

By adjusting the coat forming speed to be 0.01 to 10 μ/minute and by adjusting the amount of doping the dopants by ON/OFF switch or step by step, Eg at this junction portion could be varied such that the boundary was a surface or the boundary region was a wide transition region. The important thing was that at the boundary or the boundary region between different Egs, though it partially depends on the method of production, Ns which exists in a in hetero-junction of a single crystalline semiconductor by lattice defects, was not observed, and that notches and spikes did not exist, or did not exist substantially in the conductive band or valence band which were the edges Eg. The reason is supposed to be that Eg was decided according to the stoichiometric mixture ratio and

that neutralizer such as hydrogen and halogenide was sufficiently added. The neutralizer may be N, O, C, S, and so on as long as their energy levels are not within Eg. The above embodiment uses vacuum CVD (chemical vapor deposition) or glow discharge. In case the energy band just near the surface of a semiconductor is varied, ion implantation may be used. For example, when oxygen, nitrogen, and carbon at the concentration of 10^{15} to $10^{22}cm^{-3}$, for example, $10^{17}cm^{-3}$ were implanted in a semiconductor with the acceleration being 10 to 400 KeV, junction having continuous Eg according to Gaussian distribution in the depth of 500 to 1500Å could be obtained.

In the present invention, it is not necessary that one of the two semiconductors having different Egs is a pure semiconductor and the other is a semiconductor with a dopant. The other semiconductor may be a group III-IV compound semiconductor such as GaAlAsP. When Eg is varied by adding dopants, the semiconductors may use different amount of one dopant, for example, 10^{15} to $10^{18}cm^{-3}$ for one semiconductor and 0.01 to 30% for the other semiconductor. Further, it is needless to say that the semiconductors may use different dopants, for example, carbon of 10^{15} to $10^{22}cm^{-3}$, for example 5 to 10% for one semiconductor and nitrogen or oxygen of 10^{15} to $10^{22}cm^{-3}$, for example 5 to 10% for the other semiconductor. As can be seen clearly with the above-mentioned theory, embodiment, and r sult, according to the present invention, at or near the

junction portion of semiconductors which is very important for the operation of the semiconductors, a notch, a spike and so on and Ns peculiar to the interface are removed which are conventionally produced by junctioning the two materials having different Eg and which are not desirable. In other words, factors essentially due to making a junction with two materials, the lattice constants of which are different from each other, are removed. Therefore, the gist of the present invention is that the semiconductors are non-single-crystalline semiconductors in which lattice defects in microscopical meaning are eliminated. Since the semiconductors were such non-monocrystalline semiconductors and the recombination center was neutralized by hydrogen or halogenide, a semiconductor device in which the energy gap is varied continuously according to the stoichiometric mixture ratio, that is, a semiconductor device having continuous junction could be obtained.

Fig. 2 shows embodiments having different Egs. In (A), the junction portion is the boundary. (11) is an N type semiconductor with W-Eg (wide energy gap). (13) is a P type semiconductor with N-Eg (narrow energy gap). In the boundary region, both CB (15) and VB (15') transition smoothly. In (B), (11) is a P type semiconductor with W-Eg and (14) is a P type semiconductor with N-Eg. Similarly, the conductivity type of (C) is P. (D) shows NP junction. (E) shows smooth NP

junction. (F) shows stepwise NP junction.

CB (20) is continuous while VB(20') is substantially continuous.

Fig. 3 shows semiconductors each having two junctions. (A) shows an NPN transistor of W-L-W. In the P type region of L, recombination depending on Eg of charge can be promoted. (B) shows a PNP transistor of L-W-L. The thickness of W is 100 Å to 5 μ. (C) shows an NIP structure of L-W-L. (D) shows a PIN structure of W-W-L. The thickness of W_1 and W_2 are 10 Å to 1 μ and 100 to 5 μ, respectively. Thus, it is expected that the device is used for a photo cell or a solar cell of highly efficient conversion efficiency (15 to 50%). (E) shows an NPN transistor of W-W-L and (F) shows a PNP transistor of L-W-W.

Fig. 4 shows structures particularly useful for a photo cell or a solar cell. (A) is NPNP type where Eg (21) > Eg (22) > Eg (23) > Eg (24) and is four-layer structure of W-N. PN junction is provided in two semiconductors having different Egs to efficiently attain photoelectric conversion according to the wavelength of incident light. Eg (21) is adjusted to wavelength of 0.2 Å to 0.5 μ. Eg (24) is 1.1 eV of silicon. The thickness of semiconductors (22) and (23) is 0.01 Å to 1 μ which is thin enough compared to the diffusion length of carrier. With the above structure, the photoelectric conversion efficiency could be improved to 25 to 30%. At the temperature of 100°C, the reduction rate was only about 20 to

30%. (B) has PI_1I_2N structure. Eg (25) is also adjusted to wavelength of 0.2 to 0.5 μ. Eg (28) is 1.1 eV of silicon. Semiconductors (26) and (27) are intrinsic or substantially intrinsic to light. The same dopant is added to semiconductors (26) and (27) and the amount of the dopant of the semiconductor (26) is larger than that of the semiconductor (27). (27) is GaAlAs or SiC. Si is doped to (26) and (25). The atomic concentration of Si doped to (26) was 5 to 50% and that doped to (25) was 5 to 30%.

In the above description, the semiconductor device of the present invention comprises two semiconductors of different conductivity types having different energy bands. However, a semiconductor device also falls within the scope of the present invention which comprises two semiconductors of the same conductivity type, that is in a consistent impurity concentration of P-type or N-type, wherein the Eg thereof varies, and the variation of the Eg is either continuous or by stages.

Fig. 4(C) shows an embodiment as a light emitting element. In this case, two pockets (30) and (31) were provided with respect to an electron and a hole. Due to recombination of charge at the boundary, light of certain wavelength depending on Eg was emitted. Such a four-layer structure of P⁺P-N-N⁺ or P-P⁺N⁺N-can be embodied by just introducing or not introducing reactive gas. Thus, such an element can be mass-produced easily, and a substantially which illuminates letters, num-

bers, or simbols can be also easily made by applying a selective etch to a surface light source. In addition, the embodiment shown in Fig. 4(C) may be regarded as the combination of the embodiment shown in Fig. (E) and that shown in Fig. (F). The photoelectric conversion efficiency of the light emitting element was in the order of 3 to 10%, which is two to five times better than that of a conventional light emitting diode using monocrystalline PN junction. The element is characterized in that, by providing various values of Eg, it can emit not only light of specific wavelength but also continuous light or white light.

What should be added as the dopant may be decided with reference to Figs. 2 to 4 according to the object of the application. However, this is only means to industrially popularize the present invention.

Further, in the present embodiment, a reflection reducing film in a photosensitive device such as a solar cell is $\lambda/4$ depending on n (where n is refraction index of semiconductor), but this may be used as insulator of low clas silicon nitride or low class silicon oxide (SiO or SiO_x) by increasing sufficiently the amount of the dopant. Still further, it is needless to say that Schottky junction may be provided on the upper surface using conductive semiconductor (such as SnO_2).

As can be seen from the above description, according to

the present invention, a semiconductor is shown with silicon as its main element. However, the present invention is not limited to silicon, and the gist of the present invention is that, even the other semiconductor is made of germanium or silicon carbide, or is a compound semiconductor such as GaAs or GaAlAs, Eg can be appropriately controlled according to the applied semiconductor device. Further, it is also the gist of the present invention that, in order to practice the appropriate control of Eg, a non-single-crystalline semiconductor to which oxygen or halogenide such as chlorine was added at the concentration of 0.1 to 200% for neutralizing Ns was used as the base material, and, as necessity requires, oxygen, nitrogen, carbon, and so on stoichiometrically at the concentration of 10^{15} to $10^{22}cm^{-3}$ were added to said substrate, for example, 0.1 to 80% for carbon, 0.01 to 10% for nitrogen, and 10^{15} to $10^{20}cm^{-3}$ for carbon, so as to vary stepwise or continuously. Thus, even semiconductors having different Egs were junctioned to each other, Ns due to lattice defects and so on could be suppressed on the interface. Still further, it is also the gist of the present invention that the conductivity of a semiconductor such as P type, N type, and I type and the value of the conductivity is determined by selecting the kind of dopants and by adjusting the amount of the dopants, and that the semiconductor device was produced using glow discharge or vacuum chemical vapor deposition (CVD) in conjunction with

usage of high-frequency energy with which the semiconductor device could be continuously mass-produced. As a result, it was revealed that the thickness of one semiconductor could be freely controlled within the range of 0.01 μ to 10 μ, that dopants of a P type or an N type semiconductor could be controlled within the range of 10^{14} to $10^{22}cm^{-3}$, and that multiple junction, i.e., a plurality of PN junction, PI junction, NI junction, PNP, or PIN provided in one semiconductor, could be easily made. In addition, the present invention is remarkably characterized in that it leads to industrially totally new field of application of a semiconductor device because, according to the present invention, for example, a semiconductor device can be continuously mass-produced in the same reactor.

In particular, when roll system is applied to the production of a semiconductor device, by using print technology in mounting electrodes on the upper surface and on the lower surface of the roll, the production cost can be lowered to 1/100 to 1/10000 of the conventional production cost.

4. Brief Description of the Drawings

Fig. 1 shows energy band of conventional hetero-junction. Figs. 2 to 4 show embodiments of the present invention.

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⑭半導体装置

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明　細　書

1 発明の名称

半導体装置

2 特許請求の範囲

1 基板上に異なったエネルギバンドを有する少くとも2つの非単結晶半導体の境界または境界領域において、前記の少くとも2つの半導体の化学量論比を変えることにより、前記エネルギバンドが連続または実質的に連続した半導体層を設けることを特徴とする半導体装置。

2 特許請求の範囲第一項において、半導体の内部にはPN接合、PI接合、NI接合、PP接合、NN接合、II接合またはショットキ接合を少くとも1つ有することを特徴とする半導体装置。

3 特許請求の範囲第一項において、光照射がなされる面より遠る方向に向って光起電力を発生させる半導体層のエネルギバンドは階段または実質的に傾斜したことを特徴とする半導体装置。

3 発明の詳細な説明

本発明は異なったエネルギバンド(以下エネルギバンドまたはエネルギ・ギャップをも総称してEgと簡単のため記す)を有する2つの非単結晶の半導体の境界または境界領域において前記2つの半導体の化学量論比を変えることにより、エネルギバンドの伝導帯(以下CBという)または価電子帯(以下VBという)が連続または実質的に連続した傾斜を有する半導体層を設けることを特徴とする半導体装置に関する。

本発明は非単結晶半導体の同種または異種接合により光起電をせしめること、またはこの接合に光を照射して光起電力を発生せしめる半導体装置に関する。

本発明はかかる非単結晶半導体を可撓性フイルム状基板に設け、低コスト化連続多量生産をはんとす、半導体装置に関する。

本発明は、2つの異なったエネルギバンドを有する半導体の境界または境界領域において、PN接合、PI接合、NI接合またはショット

ヘ接合の如き異種接合、ＮＮ接合、ＰＰ接合、Ｉ１接合の如き同種接合またはその多重接合を有せしめる半導体装置に関する。

さらに本発明はかかる接合部に光を照射することにより光起電力を発生せしめ、フオトセル特に太陽電池を構成せしめること、またはかかる接合部に電流を流すことにより特定の波長の可視光または白色光を発光せしめることを特徴とした光電効果を有する半導体装置に関する。

本発明は２つの半導体の境界またはその近傍またはPN接合、PI接合、NI接合、ショットキ接合またはその多重接合等の接合またはその近傍において、境界、接合に起因する特定の界面単位を構成することなく、またはこの単位が実用上十分電気的に無視できる、いわゆる実質的に存在せぬ状態を構成する半導体装置に関する。さらにこれらのため界面単位または電荷の再結合中心を中和または相殺する水素、重水素の如き水素、または塩素、臭素の如きハロゲン化物を0.1～200%の濃度で添加された半導体装置に関する。

本発明に用いる２つの非単結晶の半導体は珪素、ゲルマニュームよりなる半導体、珪化珪素、珪化ゲルマニューム、珪化ゲルマニュームよりなるⅣ－Ⅳ族化合物半導体またはGaAs、GaAlAs、GaP、BPその他のⅢ－Ⅴ族化合物半導体である。

さらに本発明は異なつたEgを持つ上記半導体の少くとも２つを化学量論的に混合し、CBまたはVBをエネルギ的に連続せしめたものである。加えてこの境界または境界領域において化学論的にある程度定められた酸素、酸素、または窒素を添加材として添加した半導体に関する。

従来、異なつたエネルギーバンドを有する単結晶の半導体の境界を互いに接せしめた場合その境界ではいわゆるヘテロ接合（hetero-junction）を構成していた。例えば、GaPとGaAsとを接合させた場合、ともにそれらは単結晶であるためこの２つのエネルギーギャップ（以下Egという）の界面には第１図に見られる如く不整合反階型ヘテロ接合が出来てしまつた。不整合のため他の例えばGaAs AlxAs(1)とGaAs(2)との接合にはノッチ(3)、飛び(4)に加えて界面単位(5)が発生し、この界面単位（Interface statesともいう）（以下Nsという）のためにこの接合部で電子またはホールのキャリアがこのNsを介して再結合をして消滅してしまつた。

その結果、キャリアのライフタイムを減少させ、さらにこの接合を用いて特定の作用例えば光起電力を発生せしめようとした場合、光励起された電荷が光起電力を発生する前に消滅してしまうという大きな欠点があつた。加えて、電圧を印して発光させようとした場合、この単位を介して電子とホールが再結合するいわゆる間接遷移となつてしまうため、可視光等が出ず熱のみが発生してしまうという欠点が大きかつた。

さらにまたは半導体のPN接合ダイオードの特性をとした場合、逆方向特性の耐圧が著くソフトブレイクダウン型のダイオードになつてしまつた。第１図(A)はＮ－Ｐ接合の場合であるが、Ｎ－Ｎ接合である図面においてはスパイク(6)がNs(7)に加えて発生し、電子の障壁となつてその移動をさまたげてしまう大きな欠点があつた。本発明はかかるノッチ、飛び、スパイクの発生を防止する。即ち、この接合部においてエネルギーバンドにおけるC.B, V.Bの一方または双方がエネルギ的に連続的に変化せしめることを大きな目的とする。さらにこれまでヘテロ接合が必然的に界面での結晶格子不整のために存在していた不対結合手、結晶欠陥に起因するNsの発生を本発明は除去またはきわめて少くせしめたことを特徴とする。かかる構造即ち連続的な接合をエネルギーバンド的な観点において有していることによりこのエネルギーバンドの歪を利用する新しい半導体装置への応用がきわめて容易に可能になつた。

以下に本発明を実施例に基づいて説明する。

一導電型を有する珪素、ゲルマニューム、珪化珪素の如きアモルファス（同時のアモルファ

スまたは5～100Aのショートレンジオーダーでの多結晶）または100A以上の結晶性を有する多結晶構造を有する半導体（以下これらを総称して非単結晶半導体という）相互またはこの1つとGaAℓAs等の化合物半導体との各成分を化学量論的に均等に分散して設けることを本発明の特徴とする。また本発明における均等な分散とは構成元素の量論的な変動が互いに局部的に相互作用を生ぜしめる方向になることをいう。またこの変動が均等でありかつEgを決める程度に規則性または結晶性を有する非単結晶半導体であることが必要である。以下に本実施例を説明する。

本実施例においては、金属、半導体または絶縁体さらにまたはガラスまたはセラミックの如き絶縁体上に金属膜等を一部または全部に被膜化させた複合等のいわゆる固い基板またはPEPプラスチック、カプトン、マイラー、ポリイミド、セルロード、塩化ビニール、ポリウレタンその他可曲性を有するフィルム状の0.2～200μ特に1～10μの厚さの基板またはこの上面に金属膜を被膜化させた複合基板（いわゆるやわらかい基板）（以上を総称して本実施例では基板と称する）を用いた。この可曲性を有するフィルム状基板（柔かい基本）は多量生産の際はロール構造をさせることができ、かつ基板材料がきわめて安価であるという特性を有する。加えて半導体層が単結晶の場合はロール化する場合または運搬中にクラック等による信頼性をそこなう要素が発生するが本発明に用いる半導体層はアモルファスを含む非単結晶であるため弾力性に富み理想的でもつた。本発明の実施例においては、かかる基板上に例えば珪素をシラン、ジクロールシランその他の珪化物気体を用いて層状構造即ち被膜として形成せしめる。このため石英等の耐熱ガラスまたはステンレス製の反応炉の入口側にシラン、ジクロールシランの如き珪化物気体と水素または塩化水素の如きキャリアガスと、さらにリン、ヒ素の如きN型導電型の半導体中で導電性を決める不純物をフォスヒン、アルシンにより、またアルミニューム、ガリューム、ボロンの如きP型の不純物を塩化アルミニューム、塩化ガリューム、ジボランにより導入できるようにした。加えてメタン、アンモニア、酸素等炭化物、窒化物、酸化物気体を導入できるようにした。また排気は真空ポンプを用い、反応炉内を0.001torrまで真空引きができるようにした。反応炉内に基板をサセプターにて保持して入れ、反応炉を0.1～10torrに真空引きをし、そこの基板に対し1～50MHZの高周波加熱またはそれと赤外加熱とを併用し、加えさらに反応性気体を励起または分解した。高周波エネルギは電圧励起を促し、各不純物または半導体材料の結合手が十分化学的に励起されるように加えた。これら反応性気体は基板上に被膜となつて形成される。この際この被膜は基板の温度により室温～500℃まではアモルファスが、また350℃～980℃では多結晶構造となつた。基板が単結晶を有しまたその上の被膜が980℃以上ではエピタキシャル成長される場合は単結晶になるが、実験的にこれらの単結晶半導体が本発明の構造を有することは不可能でもつた。本発明は非単結晶の被膜を用いることを第1の特徴としている。この非単結晶被膜に対し、リン、ヒ素の如き半導体中でN型導電型を呈する不純物を10^{16}～$5\times10^{20}cm^{-3}$の濃度にフォスヒン（PH_3）、アルシン（AsH_3）を利用して混入させると、いわゆるN型半導体が作られる。

また他方、塩化アルミニューム（$AlCl_3$）、塩化ガリューム（$GaCl_3$）またはジボラン（B_2H_6）を同様の濃度にまで添加するとP型の半導体となる。またこの2種類の導電型の不純物を同時に混入し、さらに必要に応じて珪化物気体の導入を減少または中止して化合物半導体を形成し、この2つの半導体の間には本発明のEgが連続した境界領域を設けた。さらにこれらの不純物を全く添加しないと、真性または限りなくバックグラウンドレベルの不純物の混入によるいわゆる実質的に真性の半導体になつた。この非単結晶被膜には半導体を被膜する有利いわゆる珪素以

外に水素、重水素または塩素の四きハロゲン化物が0.2～20%の濃度で添加されている。

これらは半導体層が形成された後に残存しやすい不対結合手と結合して再結合中心の発生を抑止し、電気的に中和（不活性）する作用を有する。この水素またはハロゲン化物の半導体層の形成と同時または被膜形成後の添加は本発明を工業的に実用化するためのきわめて重要な要素であつた。

従来にあつては、被膜形成後高周波エネルギまたはマイクロ波エネルギにより不対結合手が励起され、化学的に活性の状態とした水素等を被膜中に混入して行なつた。実際には水素等の雰囲気中に基板上に半導体層が設けられた本発明装置を入れ、かかる電気エネルギを加えて水素等を活性（励起）し、さらに500℃までの温度をも加えた。

これらPまたはN型の導電型を決める不純物および水素、ハロゲン化物等不純物の添加は電気的に反応性気体を活性化と同時に水素またはハロゲン化物を活性化することにより反応する方法を本実施例では用いた。

もちろん特願昭53-86867，53-86868（本発明人の発明による）に記す如く、半導体層を形成してしまつた後に活性水素で半導体層をアニールしてもよいことはいうまでもない。

さらに本発明の実施例においては、炭素、窒素、酸素を均等に分散して半導体中に添加した。炭素はCH_4，C_2H_6を用いた。窒素はアンモニア（NH_3），ヒドラジン（N_2H_4）を、また酸素はH_2O、またはO_2とした。これら混合物としてはN_2O，NO_2，CH_3OHその他のアルコール類、CO_2，CO等を水素または塩素のキャリアガスを用いて反応炉内に導入して添加物を窒素と酸素または炭素と酸素というように2種以上添加してもよい。酸素、窒素等を単結晶の半導体被膜形成後、あとから添加しようとすると、酸化珪素（Eg=8 eV）または窒化珪素（Eg=5.5 eV）になつてしまい、絶縁物でしかなかつた。しかしこれらの添加物を珪素被膜作製と同時に電気的、または高周波またはマイクロ波による電気エネルギと熱とを併用して実施することにより添加すると、これらの添加物の化学量論比に応じて半導体は1.1 eVから3 eV（SiC），5.5 eV（Si_3N_4），8 eV（SiO_2）の中間の値を得ることができた。この被膜のEgはフオトルミネツセンスまたは光励起法により測定した。

このEgはこの化合物半導体にあつては、1.3 eV～3.5 eV（例えば、GaAs 1.4 eV，GaAlP 1.9 eV，GaP_{1-x} 2.3 eV，AlP_{1-x} 2.5 eV）の任意の値に、Ga，Al，P，Asの化学量論比を変更することにより生成した。かかる化合物半導体と他の化合物半導体または珪素等の単一元素半導体と2つの半導体は共に非単結晶構造を有しているため、界面のみにヘテロ接合にある如き特定のNsが存在することがなく、さらにエネルギーバンドは伝導帯（C．B），価電子帯（V．B）ともにある独立階段的な連続性（実質的に連続）を、またはなめらかな連続性（連続）を有して形成させることができた。

この異なる接合部でのEgの変化の程度は、被膜形成速度0.01～10 Å/分と調節し、加えて添加物のドープ量をON/OFに調整または連続的に段階を追つて調整することにより境界が面でもつたり、境界領域として巾広い遷移領域を成就した。しかし重要なことは、この異なるEgの境界またはその近傍の境界領域においては、製造方法にも依存するが、単結晶半導体のヘテロ接合にみられる格子不整等によるNsは発生せず、またEgのエツデである伝導体または価電子帯にはノツチ、スパイク等は存在しなかつた。または実質的に存在しないことが判明した。これはEgを化学量論比に従つて決めていることと同時に、水素ハロゲン等の中和剤を十分な量添加していることによるものと推察される。以上は減圧CVD（化学蒸着）法または グロー放電法を用いた実施例であるが、半導体の表面のごく近傍のエネルギーバンドを変更せしめようとする場合は、イオン注入法を用いて例えば酸素、窒素、炭素を半導体中に10^{15}～10^{20} cm^{-3} 例えば10^{17} cm^{-3}

の濃度に100～400KeVの加速により打ちこみ圧入すると500～1500Aの深さにガウス分布に従つた連続的なEgを有する半導体の接合を得ることができた。

本発明において異なるEgを有せしめる2つの半導体の一方が、純粋な半導体であつて他方が添加物の加えられた半導体のみである必要はなく、他方はⅢ－Ⅴ族の化合物半導体例えばGaAℓAsPであつてもよい。また添加物によりEgを変更しようとするならば、同種の添加物がその量を変えて例えば一方が10^{15}～$10^{18}cm^{-3}$他方が0.01～30%といつたように添加されていれば、本発明を実施させることができる。さらにまた一方は炭素を10^{15}～$10^{20}cm^{-3}$例えば5～10%、他方は窒素または酸素を10^{15}～$10^{20}cm^{-3}$例えば5～10%と添加物の種類を変えて行なえばよいことはいうまでもない。以上の理論および実施方法およびその結果より明らかな如く、本発明は半導体の動作にきわめて重要な接合部またはその近傍で異なるEgの材料を接合することにより発生する従来期待しない要素であるノンナ、スパイク等と界面固有のNsとを排除し、いわゆる異なる格子定数の材料を接合することに本質的に帰因する要素を排除したことにある。このためミクロな意味での格子不整を排除した非単結晶構造の半導体であることが本発明の重要な要旨である。かかる非単結晶構造であつて、かつ再結合中心を水素またはハロゲンにより中和したため、化学量論比に応じてエネルギーギャップを連続的に変えるいわゆる連続接合を有する半導体装置を完成させることができた。

第2図はかかる場合のEgを変えた実施例である。(A)は接合部が境界となり(11)はN型でW(WIDE)Eg(広いエネルギーギャップ)、(13)はN(NALLOW)Eg(せまいエネルギーギャップ)のP型である。境界領域(15)，(15')においてC．B(15)，V．B(15')のいずれもが連続して遷移している。(B)は同種のP型導電型であつて，(11)がW¬Egでありまた(14)はN－Egである。さらにまた(C)は同様であつて、P型の導電型である。

(D)はNP接合である。(E)はなめらかなNP接合を構成している。(F)は階段的なNP接合を構成している。

即ちC．B(20)は連続であるが、V．B(20')は実質的に連続した構成をしている。

第3図は1つの半導体中に2つの接合を有せしめたものである。(A)はW－L－WのNPNトランジスタである。LのP型領域で、電荷のEgにより決められた再結合を促進させることができる。(B)はL－W－LのPNPトランジスタである。Wの厚さは100A～5μとした。(C)はL－W－LのNIP構成であり、(D)はW－W－LのPIN構成である。W_1，W_2はそれぞれ10A～1μ、100A～5μとした。これはW領により光を屈折せしめるいわゆるフオトセルまたは太陽電池に対して高効率(15～50%)の変換効率を期待できる。(E)はW・W・LのNPN、(F)はL－W－WのPNPトランジスタである。

第4図は特にフオトセルまたは太陽電池に対して有効な構造である。(A)はNPNPであり、Eg(21)＞Eg(22)＞Eg(23)＞Eg(24)とW－N構造の4層構造である。この如くPN接合がEgの異なる2つの半導体中に設けられ、入射する光の波長に対応して効率よく光電変換がなされるようにしている。Eg(21)は波長で0.2～0.5μになるように選ばれており、またEg(24)は禁帯の1.1eVである。半導体(22)，(23)の厚さは0.01～1μであり、キャリアの拡散長に比べて十分短くとつてある。かかる構造により光電気変換効率を25～30%と改良でき、また100℃において20～30%程度減少したのみであつた。(B)はPI，IsN構造を有している。やはりEg(25)は0.2～0.5μの波長に合わせてある。またEg(26)は1.1eVの禁帯とした。半導体(26)，(27)は共に真性または実質的に真性でありともに添加物は(27)に比べて(26)を増やしたのみである。(27)はGaAℓAsまたはSiCとし、(26)はこれらSiを3～50%(25)は5～30%の原子濃度添加することにより実現した。

以上の説明においては、2つの半導体即ち異

なる導電型の半導体でありつつかつ異なるエネルギーバンド構造であることを特色として記載した。しかし同一導電型即ち一定のPまたはN型の不純物濃度であつて、かつEgが変化するがEgが連続的または階段的に変化する半導体であつても本発明の主旨するところである。

第4図(1)は発光素子とした場合である。この場合は電子およびホールに対し2つのポケット(30)(31)が設けられ、その境界での電荷の再結合によりEgに定められた波長の光を発生した。かかる4層の$P^+P^-N^-N^+$構造は単に反応性気体のガスの導入有無のみで実施できる。このため大量生産が容易であり、また面光度もさらに選択エッチを施し、文字、数字、記号を発光させる基板を作ることも容易であつた特徴を有する。加えてこの(1)は第3図(1)、(2)を互いに連結した構造とみることもできる。光電気変換効率は3～10%程度とこれまでの単結晶のPN接合を用いた発光ダイオードの2～5倍の効率を得た。このEgを種々設けることにより、特定の波長の光ではなく、連続光または白色光を発光させることもできるという特徴を有する。

この添加物は、その応用の目的により第2図～第4図において決定すればよい。しかしそれらは本発明をさらに工業的に普及せしめるための手段にすぎない。

加えて本発明において太陽電池等フオト・センシティブ・デイバイスにおける反射防止膜は$\lambda/4$でありつつn(nは半導体の屈折率)によるが、それは添加物の量をさらに十分多くして、低級酸化珪素、低級酸化珪素(SiO、またはSiOx)の絶縁体として用いてもよく、さらにこの上面に導電性半導体(SnO_2等)によるショットキ接合を設けてもよいことはいうまでもない。

以上の説明より明らかな如く、本発明は実施例において1つの半導体を珪素を中心とした半導体を示した。しかし本発明は単に珪素に限定されることなく、他方の半導体としてゲルマニューム、炭化珪素等またはGaAs、GaAlAs等の化合物半導体であつてもその応用半導体装置に

従つてEgの適当な制御を成就することにより、さらにこれを実用化するためNsを中和する水素または塩素の如きハロゲン化物が0.1～20%の濃度に添加された非単結晶半導体に基礎材料として用いたこと、さらに必要に応じてこれに酸素、窒素、炭素等の添加物を化学量論的に10^{15}～$10^{22}cm^{-3}$の範囲例えば炭素を0.1～80%、窒素を0.001～10%、さらに炭素を10^{15}～$10^{20}cm^{-3}$と階段的または連続的に変化制御して添加したこと、このため異なるEgを有する半導体が接してもその界面には電子不整等によるNsの発生を抑止できた。さらにP型、N型、I型の導電型およびその伝導度を不純物の種類およびその量を調整して添加することにより成就したこと、加えてこれら半導体装置を多量生産可能であり、かつ連続性産の可能なグロー放電または高周波エネルギを併用した減圧化 層着(CVD)を用いて作製したことにある。その結果1つの半導体の厚さを0.01μ～10μの範囲で自由に制御可能であり、PまたはN型の不純物も10^{18}～$10^{22}cm^{-3}$の最適の範囲で制御可能であり、PN接合、PI接合、NI接合またはPNP、PIN等をさらに複数接合同一半導体内部に設けた多層接合が容易に作製できることがわかつた。加えて大量生産が同一反応炉で連続的に実施できる等、工業的に全く新しい分野への道が開けたという大きな特徴を有する。

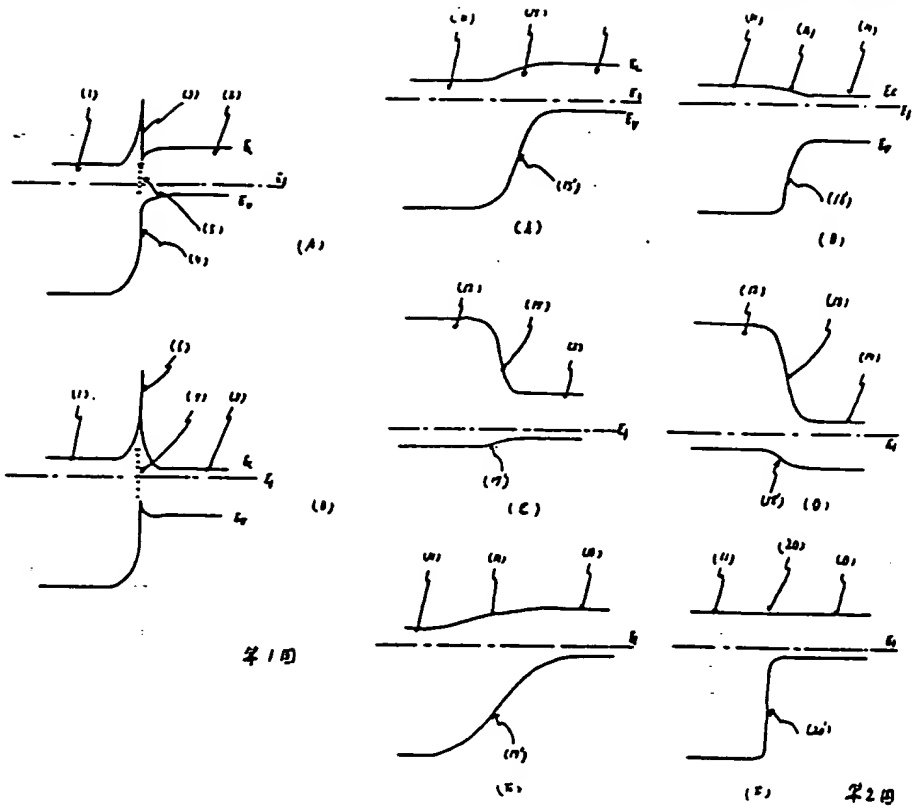
特にロール方式を用いた場合、その上下の電極を印刷技術を併用することによりこれまでの1/100～1/10000にその製造コストを下げることも可能になつた。

4.図面の簡単な説明

第1図は従来のヘテロ接合のエネルギバンド図を示す。第2図～第4図は本発明の実施例を示す。

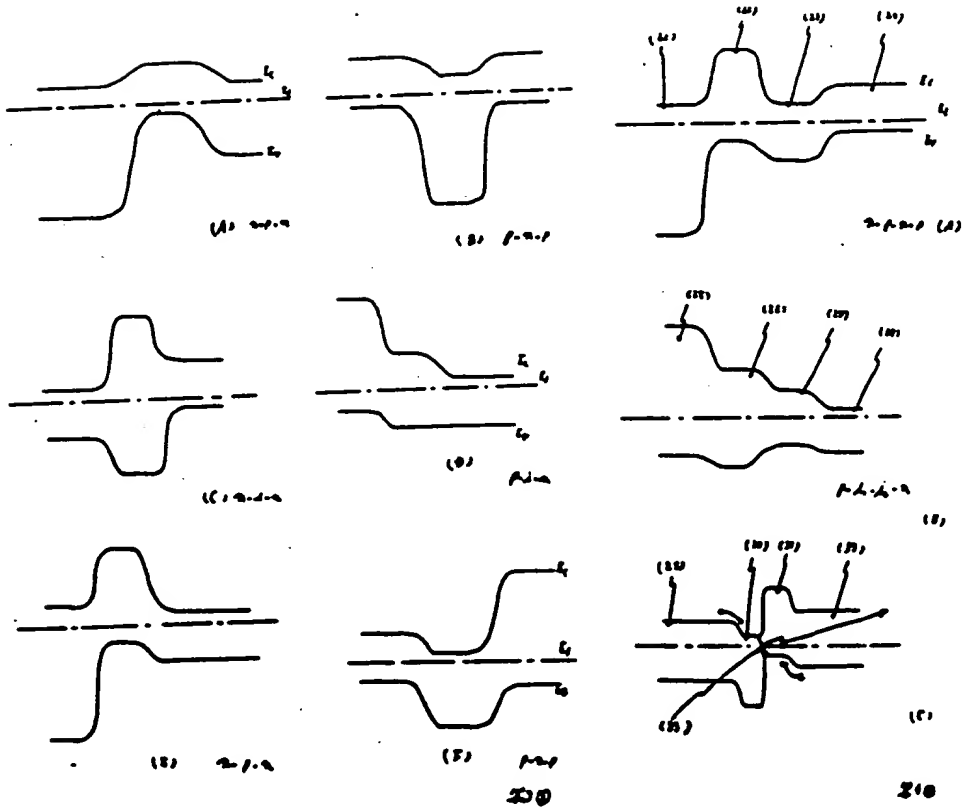
特許出願人

山崎舜平



第1図

第2図



第3図

第4図